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Fully bendable polymer light emitting devices with carbon nanotubes as cathode and anode

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Polymer light emitting devices were fabricated by roll lamination using single-walled carbon nanotubes as both anode and cathode. The devices exhibited a low turn-on voltage of 3.8 V, high brightness of 1400 cd/m^2 at 10 V and maximum efficiency of 2.2 cd/A at 480 cd/m^2. The devices are also highly transparent and exhibited very high flexibility. No failure was observed after bending the devices down to 2.5 mm radius. © *2009 American Institute of Physics*. [doi:10.1063/1.3266869]

Polymer light emitting diodes (PLEDs) have been envisioned for flexible flat panel display, signage, and lighting applications.[1,2] However, the conventional transparent electrode, indium-doped tin oxide (ITO), is brittle. ITO cracks under small tensile strain;[3] as such, PLEDs fabricated on ITO-coated flexible substrates have limited flexibility. To improve the flexibility of PLEDs, a variety of transparent conductors have been investigated as compliant anodes to replace the ITO, including solution processable conducting polymers,[4] conductive metal oxides other than ITO,[5] graphenes,[6] thin films of carbon nanotubes,[7] silver nanowires, etc.[8]

Single-walled carbon nanotubes (SWNT) thin film electrodes deposited onto various substrates via solution processes have been developed with high conductivity and high transmittance.[9,10] We have shown that ultrathin SWNT electrodes exhibit superior stretchability: these electrodes have been used to drive dielectric elastomers to electrically actuated strains up to 300% in area.[11] In addition, actuated strains of 220% have been achieved in carbon nanotube aerogels where they are the sole component.[12] The high compliancy of the SWNT electrodes arises from network formation of the high-aspect-ratio nanotubes. The electrodes consist of randomly oriented and highly interwoven carbon nanotubes. SWNT coatings have been studied as the anodes for various electronic devices including inorganic light emitting diodes (LEDs),[13] small molecule LEDs,[14] PLEDs,[15] and organic solar cells.[16]

We report the fabrication of laminated polymer light emitting electrochemical cells (PLECs) (Ref. 17) using SWNT as both cathode and anode. The devices have a simple sandwich structure of PET/SWNT/emissive polymer/SWNT/PET, wherein the emissive polymer layer contains a semiconducting polymer, an ionic conductor and a salt uniformly admixed in the polymer layer. The laminated devices are fairly transparent and highly flexible. No significant degradation on emission characteristics was observed after bending the devices down to 2.5 mm radius. The fabrication process of the polymer light emitting devices is illustrated schematically in Fig. 1(a). The devices were made by spin-coating an electroluminescent polymer layer onto a sheet of SWNT/PET and then laminating it with a second sheet of SWNT/PET. The SWNT electrodes were coated following a procedure described elsewhere onto 100 μm thick PET films.[10] The measured sheet resistance was around 500 $\Omega/\square$ with 85% average transmission in the 400–1100 nm wavelength range.

The polymer layer contained a luminescent conjugated polymer, an ionically conductive component, and a salt. PF-B was used as the blue emissive luminescent polymer. The structure of PF-B is shown in Fig. 1(b). An ethoxylated trimethylopropane triacrylate (ETT-15) was used as the ionically conductive component. Lithium trifluoromethane sulfonate (LiTf) was used as the salt. For the device fabrication, the conjugated polymers were dissolved in anhydrous, inhibitor-free tetrahydrofuran. ETT-15 and LiTf were added into the solution to afford clear solutions. The weight ratio of the polymer:ETT-15:LiTf mixture was 20:10:1. The final concentration of the conjugated polymer in the solution was 50 mg/mL. The solution was spin-coated onto the precleaned SWNT/PET at 1500 rpm. Thickness of the polymer layers was 1600 ± 100 nm measured by a Dektak profilometer. The films were stored in vacuum for two hours and another layer of SWNT/PET was subsequently laminated as the top electrode using a roll lamination machine at 120 °C.

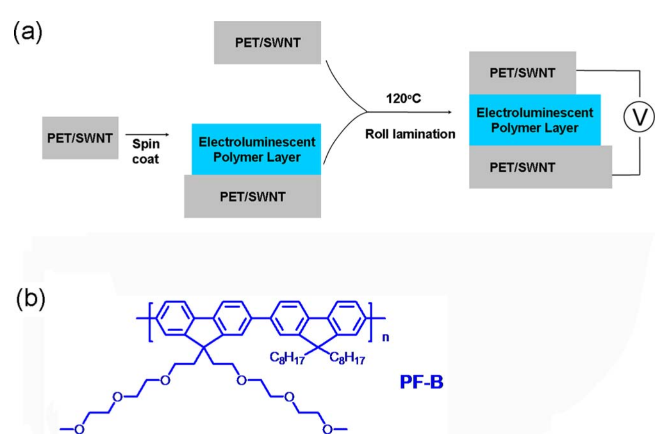

FIG. 1. (Color online) (a) Illustration of the lamination process to fabricate a polymer light emitting device and (b) Chemical structure of the blue (PF-B) emitting polymer.

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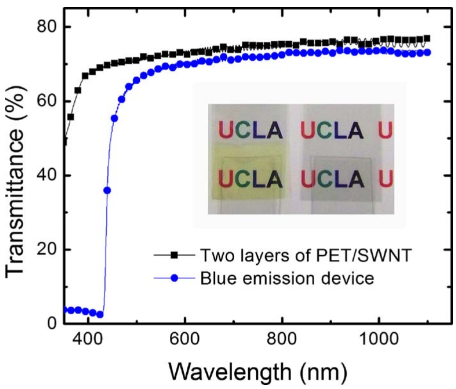

FIG. 2. (Color online) Optical transmittance spectra for two layers of SWNT/PET laminate and blue emission light emitting device. Inset shows a photograph of two layers of SWNT/PET laminate and different color light emitting devices placed on top of a sheet with color printed "UCLA" patterns.

The ultrathin SWNT electrodes are porous and have a high surface roughness of above 15 nm.[18] This roughness is detrimental to the performance of conventional PLEDs. Planarization techniques are required to smooth the SWNT surface for high efficiency light emitting devices.[18,19] In our experiments, the PLEC devices use a polymer emission layer that is more than ten times thicker than those used in the conventional PLEDs. High pressure and high temperature (above the glass transition of the polymers) were both applied during roll lamination to help form good electrical contact between the polymer and SWNT electrodes. The large thickness was found to be important to eliminate the potential electrical shorts caused by the rough SWNT layer surfaces and by the poking of long SWNTs deep into the polymer layer. At a polymer layer thickness of 1600 nm, the lamination had a 100% yield.

The laminated polymer light emitting devices with SWNT as both cathode and anode are quite transparent. The optical transmission spectra of the devices in the wavelength range of 1100–350 nm are shown in Fig. 2. The two-SWNT/PET bilayer together has a total transmission of about 73% averaged from 400 to 1100 nm. The blue emission light emitting device exhibits above 70% transmission in the wavelength range from 550 to 1100 nm, where the conjugated polymer does not absorb.

The laminated light emitting devices were tested in nitrogen filled dry box with oxygen and moisture level below 1 ppm. The current-voltage-light intensity (I-V-L) were measured with a Keithley 2400 source meter and a calibrated silicon photodetector by sweeping the applied voltage from 0 to 10 V at 100 mV increments per step. The I-V-L characteristics were shown in Fig. 3. Noticeably, the device current increased pretty linearly above a threshold voltage, which is different from the behaviors in an idea diode. This response could arise from the high series resistance by using a very thick emissive polymer layer and SWNT electrodes in our devices.[20,15] For a flat fresh device, the turn-on voltage was 3.8 V (1 cd/m^2 light emission intensity). The emission intensity reached 1400 cd/m^2 at 10 V. The maximum efficiency of the laminated devices was 2.2 cd/A at 480 cd/m^2 emission intensity. This efficiency value is on par with those reported for green emission PLEDs[15,18] using a SWNT anode and evaporated metallic cathode. In PLECs, electrochemical reactions occur when a sufficient voltage is applied; the light

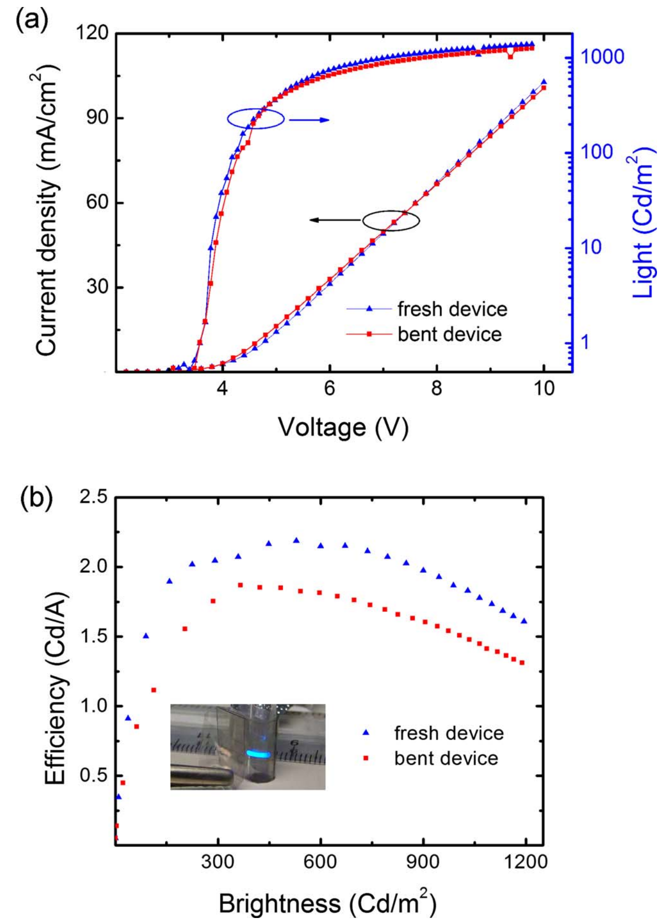

FIG. 3. (Color online) (a) Current and light emission intensity of the blue emission device at flat state before and after being bent to a 2.5 mm radius. (b) Efficiency of the flat device before and after being bent to a 2.5 mm radius (inset shows an emission photo at 6 V of the blue emission device wrapped around a 5 mm diameter glass tube).

emitting conjugated polymer becomes *n*-doped along the cathode side and *p*-doped along the anode side.[21,22] The junction formation allows the use of high work function cathode and the use of thicker active polymer films without impairing the device performance.

The blue emission devices had superior flexibility and could be bent to a radius of curvature of 2.5 mm without failure. No significant change in light emission intensity and uniformity was observed after the devices were bent to 2.5 mm radius. The inset in Fig. 3(b) shows a photo of one device wrapped around a glass tube with a 5 mm diameter. Bending down to 2.5 mm radius curvature did not significantly deteriorate the emission characteristics. For the device recovered from the 2.5 mm radius bending, the turn-on voltage remains as 3.8 V. Slight decrease in emission intensity and efficiency were observed: the light intensity at 10 V decreases to 1260 cd/m^2 and the maximum efficiency decreases to 1.9 cd/A (at 360 cd/m^2).

The flexibility of the laminated light emitting devices is much higher than those achieved in PLEDs using ITO or a conducting polymer as one or both of the opposite electrodes. The maximum bending curvature was limited to a 7 mm radius when ITO was used as the electrodes.[23] Conducing polymers are more compliant than ITO. With a conducting polymer employed as the anode and a metallic layer as the cathode, cracks were found to initiate along the cath-

ode side when the devices were bent to a 3 mm radius.[24] In addition to its high compliancy, the SWNT electrode is also more conductive than any of the conducting polymers used so far for PLED electrodes. The widely used transparent conducting polymers, poly-3,4-ethylenedioxythiophene-polystyrenesulfonate, has a conductivity <100 S/cm. Treatment with high boiling point additives can raise the conductivity up to 500 S/cm,[25] which is still three times lower than that of SWNT electrodes. SWNT electrodes have also been shown excellent stability in repeated bending. Bending between flat and a 12.5 mm radius curvature for over 10 000 cycles negligibly changed the surface resistance of the SWNT electrodes.[19]

In summary, SWNT electrodes have been used as both the cathode and anode for blue emission polymer light emitting devices. The devices had a simple layered structure and were fabricated by a roll lamination process. The devices are highly transparent with transmittance above 70% in the wavelength range where the emissive polymer does not absorb. The devices showed good electroluminescent performance: low turn-on voltage (3.8 V), high efficiency (2.2 cd/A at 480 cd/m^2), and high brightness (1400 cd/m^2 at 10 V). Such devices are also highly flexible and can be bent to a 2.5 mm radius without significantly degrading the emission characteristics.

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